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In situ biaxial texture analysis of MgO films during growth on amorphous substrates by ion beam-assisted deposition

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ABSTRACT

We used a kinematical electron scattering model[1] to develop a RHEED based method for performing quantitative analysis of mosaic polycrystalline thin film in-plane and out-of-plain grain orientation distributions. RHEED based biaxial texture measurements are compared to X-Ray and transmission electron microscopy measurements to establish the validity of the RHEED analysis method. MgO was grown on amorphous Si_3N_4 by ion beam-assisted deposition (IBAD) using 750 eV Ar^+ ions and MgO e-beam evaporation. The ion/MgO flux ratio was varied between 0.66 and 0.42. *In situ* RHEED analysis reveals that during nucleation the out-of-plane orientation distribution is very broad (almost random), but narrows very quickly once well-oriented grains reach a critical size. Under optimal conditions a competition between selective sputtering and surface roughening yields a minimum out-of-plane texture at about 100 Å, which degrades with increasing film thickness. The narrowest in-plane orientation distribution (5.4° FWHM) was found to be at an ion/MgO flux ratio between 0.55 and 0.51, in good agreement with previous experiments. The systematic offsets between RHEED analysis and X-ray measurements of biaxial texture, coupled with evidence that biaxial texture improves with increasing film thickness, indicates that RHEED is a superior technique for probing surface biaxial texture.
Keywords: IBAD, MgO, biaxial texture, RHEED, ion beam-assisted deposition

1. INTRODUCTION

Biaxially textured MgO is technologically interesting since it provides a suitable path for silicon integration of single crystal-like films for many important perovskite oxide thin film materials. This is accomplished by using ion beam assisted deposition (IBAD) to create biaxially textured films (polycrystalline films with a preferred in-plane and out-of-plane grain orientation) on amorphous substrates. Film functionality often depends on both the out of plane grain orientation distribution (FWHM is designated as $\Delta\omega$) and in-plane grain orientation distribution (designated as $\Delta\phi$). Some highly aligned biaxially textured oxide materials can exhibit similar functionality to single crystalline films. For example, biaxially textured superconductors like $YBa_2Cu_3O_{7-x}$ have been reported to have critical current densities approaching those of single crystalline films, while randomly oriented polycrystalline films exhibit much lower critical current densities. Biaxially textured piezoelectric films with 90° domain rotations are also expected to have flexing characteristics similar to those of single crystalline piezoelectric films, while randomly oriented polycrystalline piezoelectric films experience significant degradation of translational range of motion. Incorporation of biaxially textured piezoelectric films with silicon integrated circuits would enable new types of actuators for micro electrical mechanical systems (MEMs). Previous work has shown that piezoelectric materials like $Pb(Zr,Ti)O_3$ and $BaTiO_3$ can be deposited heteroepitaxially onto single crystal MgO (001)[2,3] and even Si (001)[4]. However, conventional silicon integrated circuit processing employs extensive hydrogen passivation, which degrades ferroelectrics like $Pb(Zr,Ti)O_3$ and $BaTiO_3$. It is therefore desirable to monolithically integrate piezoelectric materials following integrated circuit fabrication. Wang et al. demonstrated that IBAD MgO grown on amorphous Si_3N_4 develops narrow biaxial texture in films only 11 nm thick[5]. By eliminating the requirement for a pre-existing heteroepitaxial template, IBAD provides an opportunity to incorporate piezoelectric materials on top of amorphous dielectric films in silicon integrated circuits during the backend processing.

The performance of piezoelectric MEMs is likely to depend on the biaxial texture inherited from the MgO substrate. Previous efforts to optimize the biaxial texture of IBAD MgO have been impeded by the *ex situ* nature of conventional biaxial texture analysis techniques (transmission electron microscopy - TEM or X-ray diffraction). Because the biaxial texture develops within 11 nm of growth, X-ray diffraction cannot resolve crystallographic texture unless the X-ray source has synchrotron brightness. For these same reasons, the IBAD biaxial texturing mechanisms are also poorly understood. To circumvent these obstacles we have developed a reflection high-energy electron diffraction (RHEED) based method for quantitative *in situ* biaxial texture analysis of MgO. Because RHEED is sensitive to films as thin as 30

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angstroms thick, we have the capability of analyzing the biaxial texture development during grain growth, film coalescence, and film growth. This analysis capability enables greater understanding of IBAD MgO biaxial texture development and how to optimize the MgO biaxial texture.

2. EXPERIMENTAL APPROACH AND MODEL-BASED ANALYSIS

Our RHEED based biaxial texture analysis employs a previously reported kinematical electron scattering calculation[1]. These calculations predict that spot shapes are sensitive to the film microstructure. Diffraction spot width and height are inversely proportional to the grain size and electron penetration depth, respectively. The width of the diffraction spot in the direction perpendicular to the location of the through spot is directly proportional to the out-of-plane grain orientation distribution ($\Delta\omega$). We therefore characterize RHEED patterns (whether calculated using a computer simulation or from an experiment) by cutting across the diffraction spots along the previously mentioned directions and measuring the FWHM of these cuts, as shown in Figure 1. Several spots can be analyzed simultaneously, and then compared to calculated RHEED patterns using a lookup table. The film grain size, electron penetration depth, and $\Delta\omega$ are determined by searching the lookup tables for the simulated film values that yield the smallest error between the calculations and experiment. This technique is not very sensitive to the film in-plane orientation distribution, which is measured using RHEED in-plane rocking curves, as previously described[1].

To experimentally measure in-plane orientation distribution ($\Delta\phi$), the FWHM of several in-plane rocking curves[6] from different diffraction spots, are measured simultaneously and compared to the FWHM of calculated in-plane rocking curves using a lookup table. The in-plane orientation distribution is determined by searching the lookup table for the simulation that has RHEED in-plane rocking curves that most closely match the experimental rocking curves for all spots. The FWHM of the in-plane rocking curves are highly correlated with the in-plane orientation distribution, however, the rocking curve FWHM is also convoluted with the grain size and out-of-plane orientation distribution. Therefore, to accurately measure in-plane orientation distribution using rocking curves, the grain size and out-of-plane orientation distribution is first measured using single image analysis as described above. The subsequent comparisons between the experimental and simulated FWHM of the in-plane rocking curves in the lookup tables are restricted to simulations with the previously measured grain size and electron penetration depth.

Experimental RHEED in-plane rocking curves and single image analyses were performed on eight IBAD MgO samples grown at Los Alamos National Laboratories. A single crystal of MgO was also analyzed for reference. The IBAD MgO films were ~ 11nm thick, deposited on amorphous Si_3N_4/Si (001). RHEED measurements were done at 25 kV and 2.6 degrees incidence angle. Bragg spots along the (00), (02), and (04) Bragg rods, as shown in Figure 1, were used in the RHEED analysis. In-plane orientation distributions were measured using either grazing incidence X-ray diffraction or TEM. Some samples were evaluated using TEM to determine the average grain size, while the out-of-plane orientation distributions were evaluated using X-ray rocking curves. Because the IBAD MgO layer is only 11 nm thick, X-ray scattering was performed using synchrotron radiation for the out-of-plane rocking curves.

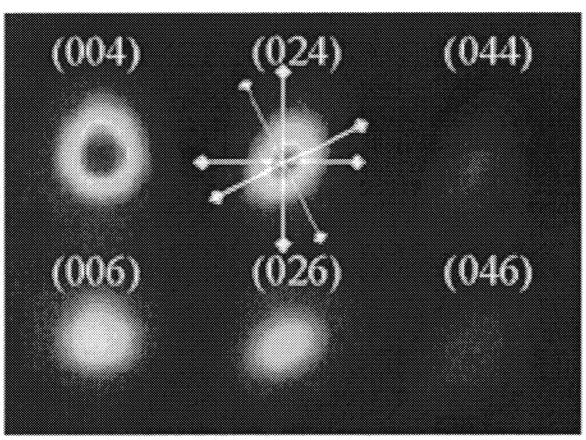

Figure 1: RHEED image of IBAD MgO. The relevant diffraction spots are indexed and the single image analysis diffraction spot measurement directions are shown on the (024) diffraction spot.

In order to investigate biaxial texture development during IBAD MgO growth we performed real time RHEED measurements. Ion irradiation during MgO growth was performed with 750 eV Ar+ ions at 45° incidence angle. MgO was simultaneously deposited, using e-beam evaporation, with evaporation rates between 2.1 Å/s and 3.3 Å/s, as measured by a quartz crystal oscillator. Although the ion flux was not directly measured, the ion/MgO flux ratio was determined by comparing the critical MgO deposition rate (the MgO deposition rate at which there begins to be net film growth) found in our experiments with the critical ion/MgO flux ratio found by C.P. Wang[7]. Film thickness was estimated by assuming the optimal thickness of the most highly biaxially textured films was 10 nm[7], then scaling the growth rate of other films with the MgO deposition rate. Using this method, the film thickness should be accurate to within 20%. Once the films were grown to the optimal thickness, determined by when the (004) diffraction spot reached maximum intensity[7], an in-plane rocking curve was taken to measure in-plane orientation distribution. For investigation of

		Grain Size (nm)		Out of Plane Orientation Distribution (degrees)		
Sample	TEM	Single Image	In-Plane	X-Ray	Single Image	In-Plane
M306	6.6	9.5	33.9	7.1	5.6	8
M307	6.2	9.2	28.2	6.4	6.2	8
M312	7.0	11.0	34.3	6.0	5.0	9

Table 1: Comparison of measurements made for grain size and out of plane orientation distribution ($\Delta\omega$) using X-ray/TEM and RHEED methods

biaxial texture development of thicker films, either a homoepitaxial layer of MgO was deposited at 600° C or an additional 100 Å of IBAD MgO was deposited.

RHEED images were acquired using a 16 bit, 1024x1024 pixel CCD camera. Because of the high resolution and dynamic range required for this experiment, images could be acquired every 5 seconds, which corresponds to about one RHEED image per monolayer of film growth.

3. RESULTS AND DISCUSSION

3.1 RHEED based measurement validation

Measurements of out-of-plane orientation distribution ($\Delta\omega$) and grain size (L) using TEM, X-ray diffraction, and RHEED are summarized in Table 1. Rocking curve and single image analyses both generally yield the correct relative grain sizes and out-of-plane orientation distributions, however, the rocking curve measurements differ from those measured with TEM and X-ray diffraction. This is attributed to the convolution of these parameters with the in-plane orientation distribution. Single image analysis is predicted by the simulation to be independent of the in-plane orientation distribution and also yields results that are very similar to the values from TEM and X-ray measurements. For this reason, only values for grain size and out-of-plane orientation distribution measured by single image analysis are used in the in-plane rocking curve lookup tables.

Figure 2 is a scatter plot of in-plane orientation distributions measured by RHEED and also by TEM or X-ray scattering. The data are well represented by a linear fit. However, there is a systematic offset between the RHEED analysis results and the TEM and X-ray diffraction measurements. X-ray scattering probes the entire film thickness rather than the surface, so it measures the in-plane orientation distribution averaged throughout the film thickness. RHEED is much more surface sensitive and therefore measures the in-plane orientation of only the topmost film layers. During IBAD MgO growth, the in-plane orientation distribution narrows with increased film thickness. Therefore it is reasonable to expect that RHEED would measure narrower in-plane orientation distributions than X-ray diffraction. The results are analogous for RHEED measurements of out-of-plane orientation distributions. Out-of-plane orientation distributions narrow with increased film thickness. The surface sensitivity of RHEED versus the film average measurement of X-ray diffraction explains why RHEED measurements are narrower for out-of-plane distributions (see Table 1). In general, RHEED based microstructure analyses yield more accurate estimates of surface biaxial textures than does X-ray diffraction.

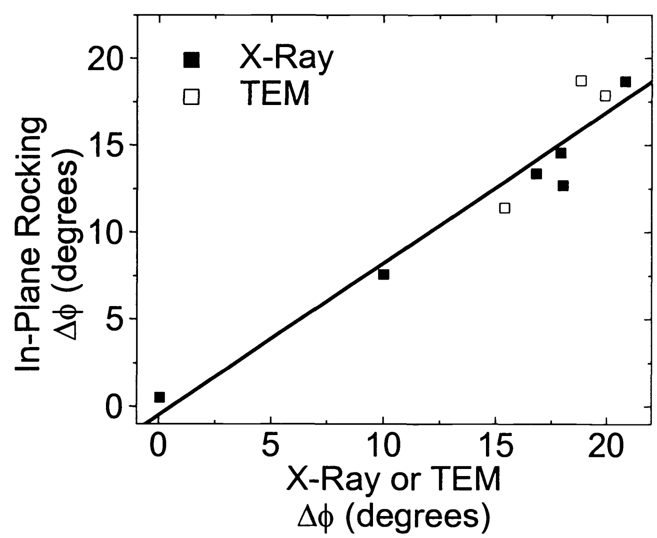

Figure 2: In-plane orientation distribution ($\Delta\phi$) FWHM as measured by RHEED analysis vs. $\Delta\phi$ measured using either X-ray diffraction or TEM

3.2 *In situ* RHEED based biaxial texture analysis

Using our RHEED based methods we have measured out-of-plane orientation distributions

($\Delta\omega$) and in-plane orientations distribution ($\Delta\phi$) during IBAD MgO growth and subsequent MgO homoepitaxy. Figure 3 summarizes the measurements for $\Delta\omega$ as a function of approximate film thickness. Measurements below 3 nm film thicknesses are not reported because the RHEED pattern was irresolvable.

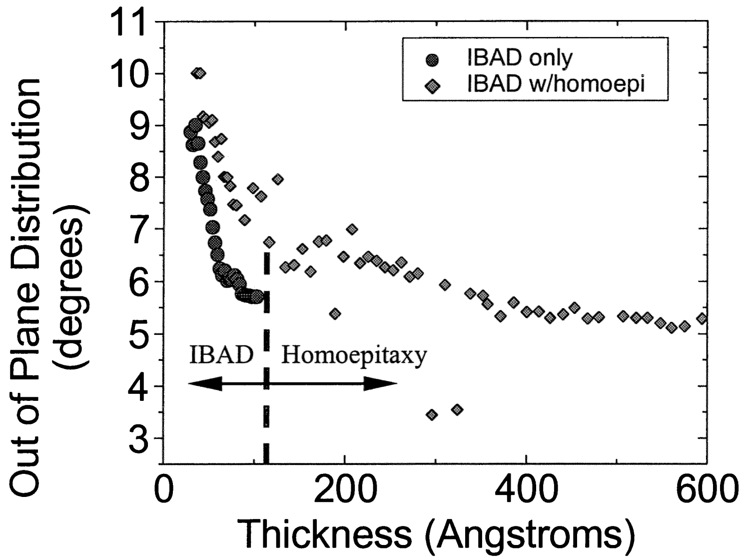

Figure 3: Out-of-plane orientation distribution as a function of film thickness. Growth from zero to ~100 angstroms is with IBAD. Subsequent growth is homoepitaxy at 600° C.

One dramatic result is that, under these growth conditions, the out-of-plane orientation distribution ($\Delta\omega$) starts out very broad, and then decreases during IBAD growth. It has been previously suggested that during IBAD MgO growth the grains initially nucleate with a narrow out-of-plane orientation distribution. However, it is evident that the grains nucleate with a very broad out-of-plane orientation distribution. Homoepitaxy of MgO at 600° C and 1 Å/s causes the out-of-plane orientation distribution to slowly decrease. A similar phenomenon has been observed for the in-plane orientation distribution. Figure 4 plots the in-plane orientation distribution as a function of film thickness. There occurs a significant decrease in the in-plane distribution simply by heating the 10 nm IBAD MgO film to 600° C. Ion bombardment creates film defects and may even locally amorphize the IBAD MgO film. It is possible that at high temperatures the less damaged grains will grow into the more damaged grains following a mechanism similar to that proposed by Dong and Srolovitz[8]. In this growth model the more damaged, maybe even locally amorphous, grains will recrystallize and adopt the orientation of the least damaged grains. The surface energy associated with grain boundaries, which increases with temperature, may also drive the more aligned grains to grow into the misaligned ones. During an additional 500 Å of homoepitaxy the in-plane orientation distribution decreased to 9.0° FWHM. We note that since both the in-plane and out-of-plane orientation distributions decrease during homoepitaxial growth, previously reported X-ray analysis of biaxial texture of MgO films that have an additional homoepitaxial layer to enable measurements with a lab based X-ray source are not quantitatively representative of the IBAD MgO film texture.

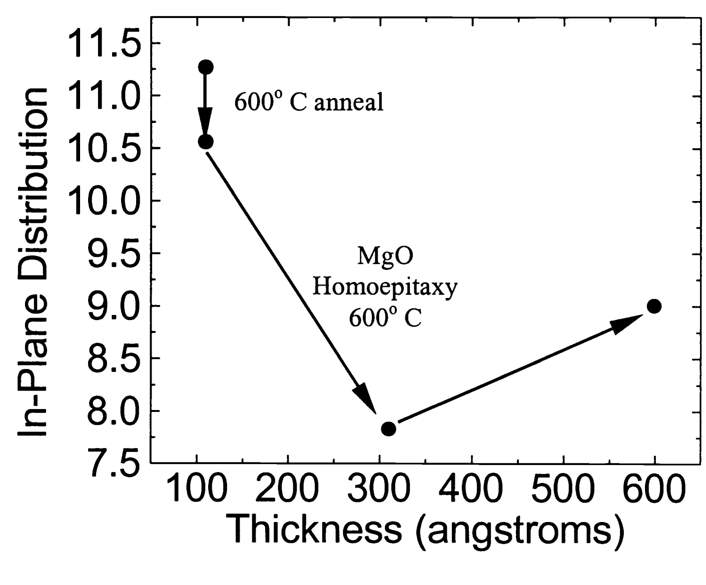

Figure 4: In-plane orientation distribution for MgO as a function of film thickness. MgO was grown using IBAD to 100 angstroms. Subsequent growth is homoepitaxy at 600° C. Arrows are a guide to the eye.

In situ RHEED analysis has also given new insights into the biaxial texture development as a function of ion/MgO flux ratio. The RHEED image sequence in Figure 5 shows a typical RHEED pattern development during IBAD MgO growth for the range of ion/MgO flux ratios investigated. The broad rings in Figures 5a and 5b are characteristic of random out-of-plane oriented polycrystalline films. These rings are

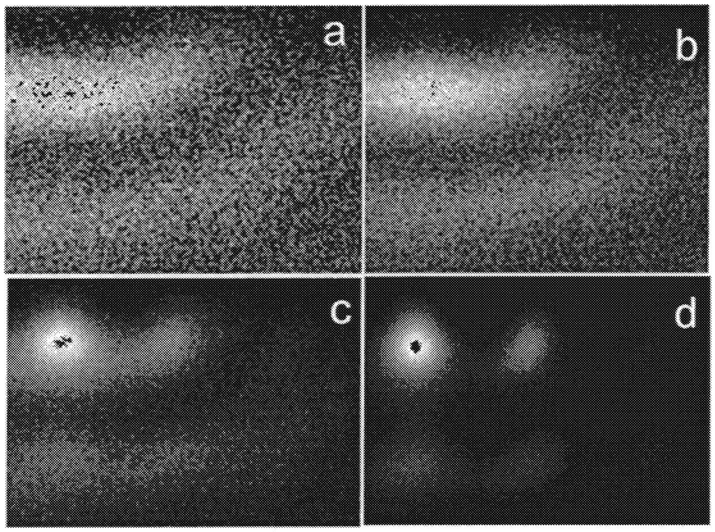

Figure 5: RHEED images from IBAD MgO growth. Thickness differences between images correspond to about one monolayer. Final film thickness for image d is approximately 3 nm.

consistent with MgO crystal structure and all contributions from the α-Si_3N_4 substrate have been subtracted out. Subsequent images in Figures 5c and 5d show a rapid decrease in out-of-plane orientation distribution, as evidenced by the disappearance of the rings. The difference in film thickness between each image corresponds to about one monolayer, with the thickness of image d being about 3 nm. Before image d, the RHEED spots cannot be analyzed with the current RHEED model because the calculations are only valid for relatively narrow orientation distributions[1]. Figure 6 summarizes the RHEED based measurements of out-of-plane orientation distributions during IBAD MgO growth. For high ion/MgO flux ratios, the out-of-plane distribution starts out broad and then decreases, while for low ion/MgO flux ratios the out-of-plane distribution is initially narrow, but consistently degrades. Figures 5 and 6 together give a fairly clear picture of texture development during the nucleation stage.

When grains first nucleate they are randomly oriented out of plane (and therefore in-plane). As the grains reach a critical size, the biaxially aligned grains are able to grow quickly, while the misaligned grains are eroded. If the ion/MgO flux ratio is too high, although the misaligned grains are selectively eroded, even the properly aligned grains are highly damaged, resulting in a rough surface (see Figure 7), preventing a narrow out-of-plane distribution from being established. At low ion/MgO flux ratios the aligned grains are the first to attain the critical grain

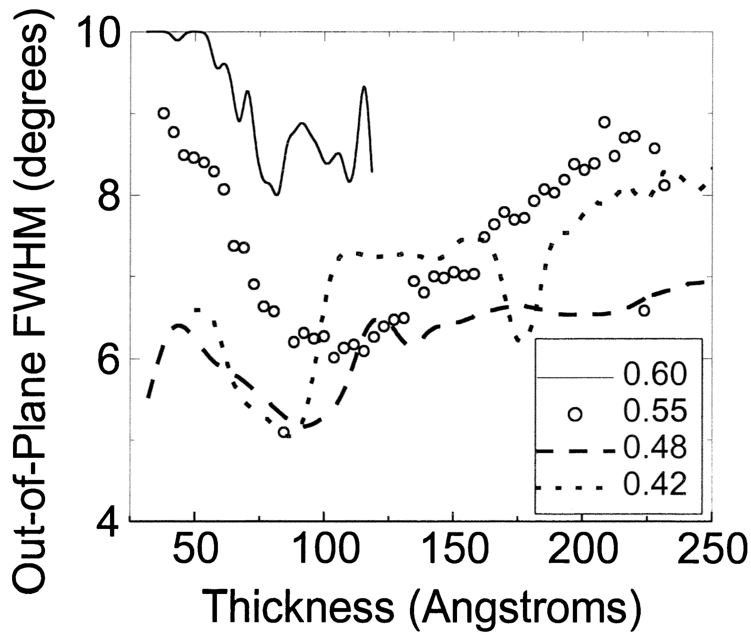

Figure 6: Out-of-plane orientation distribution as a function of thickness for IBAD MgO growth with different ion/MgO flux ratios.

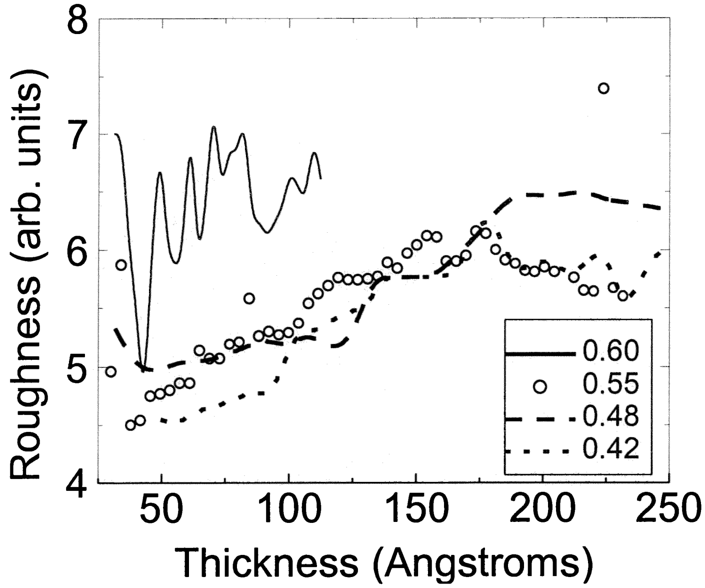

Figure 7: RHEED measured surface roughness as a function of film thickness for IBAD MgO growth with different ion/MgO flux ratios.

size so the initial texture is optimal, however, the high MgO flux provides enough material to allow even misaligned grains to attain a critical size and grow, i.e. the ion bombardment can not selectively etch the misaligned grains fast enough. For the optimal biaxial texture development (ion/MgO flux ratio of 0.55) a balance is found between growing slow enough to allow for selective etching of misaligned grains, but fast enough to avoid excessive ion damage and surface roughening. In this case the out-of-plane texture is initially broad, but rapidly decreases to a minimum at the thickness where the in-plane texture also achieves a minimum (~ 100 Å).

For all ion/MgO flux ratios the film gradually roughens with film thickness (see Figure 7). C.P. Wang et al. observed in TEM images that IBAD MgO grows cube on cube as opposed to uninterrupted columnar growth[5]. Ion damage drives grain renucleation throughout growth. By forcing grains to renucleate on undulated surfaces the out-of-plane distribution is broadened with film thickness. Even under the optimal out-of-plane texturing conditions, film roughness eventually overcomes the selective ion sputtering driving out-of-plane alignment, resulting in out-of-plane orientation distribution degradation. The out-of-plane misorientation decreases the effectiveness of in-plane alignment mechanisms and yields a broader in-plane orientation distribution as well.

The optimal ion/MgO flux ratio was determined by growing a series of IBAD MgO films with varying ion/MgO flux ratios from 0.66 to 0.42 and measuring the in-plane distribution at the film thickness where the (004) diffraction spot obtained its maximum intensity. The in-plane distributions from these experiments, as well as data from previous work at Stanford[7], using 700 eV Ar+ ions, are plotted together in Figure 8. By forcing the critical ion/MgO flux ratios to align (the ion/MgO flux where net growth is barely achieved), the optimal ion/MgO ratios between the two experimental sets are automatically aligned. This affirms the consistency of the two sets of experiments. However, our in-plane measurements are broader than the previous results at 0.66 ion/MgO flux ratio. The in-plane distribution in our experiments also shows a more rapid broadening than previously reported as the ion/MgO flux ratio increases. Because they were forced to measure biaxial texture with lab based X-Ray diffraction it was necessary to grow an additional 600 Å homoepitaxial layer, at 600° C, to attain enough signal for an accurate measurement. We have previously shown that biaxial texture improves with elevated temperature homoepitaxy. Therefore it is not surprising that we measure in-plane orientation distributions that are broader than previously expected. It is

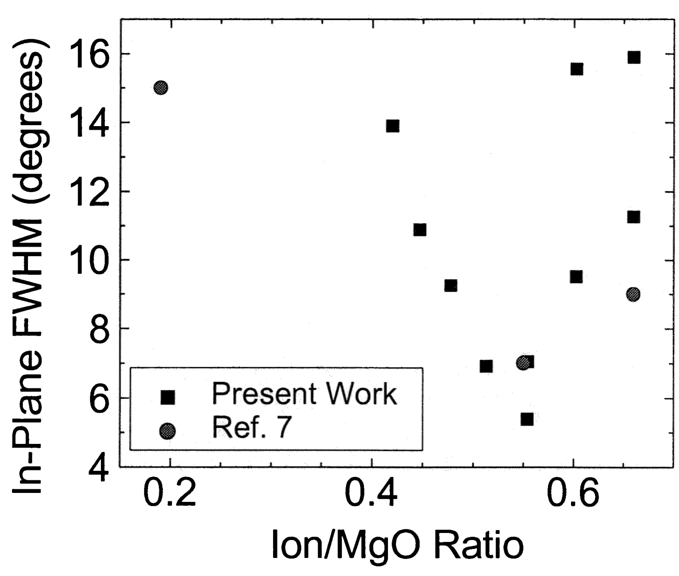

Figure 8: In-plane orientation distribution as a function of ion/MgO flux ratio.

worth noting that there seems to be no difference between our measurement of an IBAD only film and the measurement made on a film with an additional 600 Å homoepitaxial layer. We expect that the improvement accompanying homoepitaxy is most significant for highly damaged films where the properly aligned grains have an opportunity to grow into their misaligned neighbors. Optimal films have the narrowest orientation distribution and subsequently would be the least damaged. Additional homoepitaxy would not necessarily change the in-plane texture for these films, however, the out-of-plane texture may benefit from the smoothing effect of high temperature homoepitaxy.

4. CONCLUSION

We have developed a RHEED based method for quantitative biaxial texture measurement of MgO. *In situ* RHEED analysis reveals that during nucleation the out-of-plane orientation distribution is very broad (almost random), but narrows very quickly once well-oriented grains reach a critical size. Subsequent development of out-of-plane texture depends strongly on the ion/MgO flux ratio. Under optimal conditions a competition between selective sputtering and surface roughening yields a minimum out-of-plane texture at about 100 Å, which degrades with increasing film thickness. The narrowest in-plane orientation distribution (5.4° FWHM) was found to be at an ion/MgO flux ratio between 0.55 and 0.51, in good agreement with previous experiments. Homoepitaxy of MgO improves the biaxial texture of the IBAD layer, making X-ray measurements of IBAD films with an additional homoepitaxial layer not quantitatively representative of the IBAD layer. The systematic offsets between RHEED analysis and X-ray measurements of biaxial texture, coupled with evidence that biaxial texture improves with increasing film thickness, indicates that RHEED is a superior technique for probing surface biaxial texture. This technique provides novel information about the biaxial texture development and will facilitate rapid investigation of biaxial texturing mechanisms and biaxial texture optimization.

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